

**EUROPEAN PATENT APPLICATION**

Application number: 79302565.1

Int. Cl.<sup>3</sup>: **C 22 B 3/00**  
**B 01 J 20/32, C 07 F 7/08**

Date of filing: 14.11.79

Priority: 15.11.78 GB 4464278

Date of publication of application:  
 28.05.80 Bulletin 80/11

Designated Contracting States:  
 BE DE FR GB IT NL

Applicant: The British Petroleum Company Limited  
 Britannic House Moor Lane  
 London EC2Y 9BU(GB)

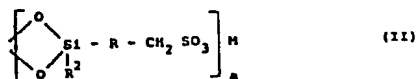
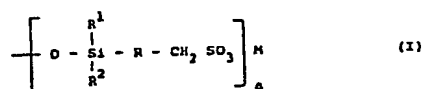
Inventor: Hancock, Ronald David The British  
 Petroleum  
 Company Limited Chertsey Road  
 Sunbury-on-Thames Middlesex, TW16 7LN(GB)

Inventor: Kirk, Jennie Marie The British Petroleum  
 Company Limited Chertsey Road  
 Sunbury-on-Thames Middlesex, TW16 7LN(GB)

Representative: MacLeod, Malcolm et al,  
 BP TRADING LIMITED Patents and Licensing Division  
 Chertsey Road  
 Sunbury-on-Thames, Middlesex, TW16 7LN(GB)

Removal of metals from solution.

Metals are removed from aqueous or organic solution  
 by contacting the solution with a product, derived from an  
 inorganic oxide containing surface hydroxyl groups, e.g.,  
 silica, containing groups of general formulae (I) and/or (II).



R is a divalent radical containing up to 20 carbon atoms,  
 R<sup>1</sup> and R<sup>2</sup> are halogen atoms, organic radicals containing up  
 to 20 carbon atoms, or hydrolysis products thereof, M is a  
 metallic or hydrogen ion and (a) is an integer corresponding  
 to the valency of M.

Suitable metals for removal include copper, silver,  
 rhodium, lead, uranium, palladium, cobalt and mercury.

The process may be used to recover wanted metals or to  
 remove contaminants.

EP 0 011 484 A1

1.

REMOVAL OF METALS FROM SOLUTION

The present invention relates to the removal of metals from solution and in particular to the removal of calcium, iron, copper, rhodium, silver, mercury and uranium from solution.

5       As a result of previous refining processes, traces of copper are sometimes present in distillate fuels such as automotive and aviation gasolines and aviation kerosines. Copper is undesirable because it is an oxidation catalyst which promotes the formation of gums and resins which affect  
10 the performance of an engine. It is current practice to combat the adverse effect of copper by adding a copper deactivator to the fuel.

When mercury is employed in processing operations it is necessary owing to its toxic nature to reduce to  
15 a minimum the quantities that are discharged to the environment in whatever form, including liquid effluents that are discharged to water courses. This is of particular importance in the manufacture of chlorine and caustic soda by the electrolysis of brine in mercury  
20 cathode electrolytic cells where the depleted brine leaving the cells contains a small concentration of mercury, usually between 2 and 10 mg/litre, either in the form of elemental mercury or mercury compounds. If this depleted brine is discharged to waste the value of the lost mercury is  
25 significant and the receiving water course may be polluted

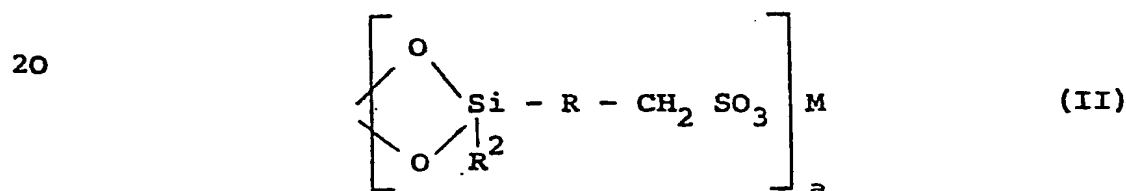
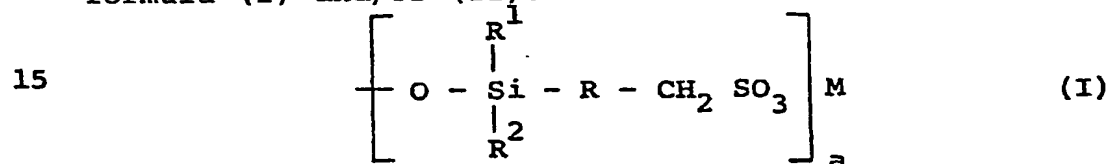
1.

with mercury compounds to an unacceptable level.

In the photographic industry it is desirable on economic grounds to remove and recover silver from residues.

Other situations in which it is desirable or essential to remove soluble metal ions from solution include the softening of water, i.e., the removal of calcium ions, and the hydrometallurgical processing of mineral ores and metal concentrates.

Our co-pending British Patent Application No. 35566/78 (BP Case No. 4620) discloses a process for the production of a product derived from an inorganic oxide containing surface hydroxyl groups, containing groups of general formula (I) and/or (II):



wherein R is a divalent radical containing up to 20 carbon atoms,  $\text{R}^1$  and/or  $\text{R}^2$  are halogen atoms, organic radicals containing up to 20 carbon atoms, or hydrolysis products thereof, M is a metallic or hydrogen ion and (a) is an integer corresponding to the valency of M.

Suitable inorganic oxides containing surface hydroxyl groups include alumina, titania, zirconia, glass, sepiolite and zeolitic molecular sieve. Preferably the inorganic oxide is silica and more preferably silica gel. In addition, mixtures of inorganic solids may be used. Unless they have been subjected to severe treatment, e.g., heating above 1000°C, commercial silicas contain surface hydroxyl

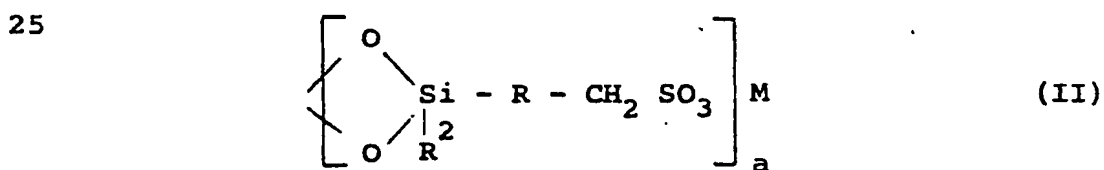
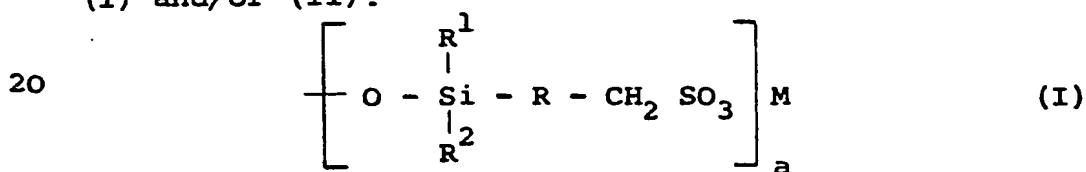
groups.

$R^1$  and/or  $R^2$  in the compounds of formulae (I) and/or (II) may be halogen atoms, alkyl, aryl, aryloxy or alkoxy radicals or hydrolysis products thereof, and may be the same or different. Preferably  $R^1$  and/or  $R^2$  are alkoxy groups containing 1-3 carbon atoms or hydrolysis products thereof. Most preferably they are identical groups.

R is preferably an alkylene group containing up to 10 carbon atoms, most preferably a di- or tri-methylene group.

We have now discovered that this product is suitable for use in the removal of metals from solution.

Thus according to the present invention there is provided a process for the removal of metals from solution which process comprises contacting the solution with a product, derived from an inorganic oxide containing surface hydroxyl groups, containing groups of general formulae (I) and/or (II).



wherein R is a divalent radical containing up to 20 carbon atoms,  $R^1$  and/or  $R^2$  are halogen atoms, organic radicals containing up to 20 carbon atoms, or hydrolysis products thereof, M is a metallic or hydrogen ion and (a) is an integer corresponding to the valency of M.

The metals may be removed from both aqueous and non-

aqueous, e.g., liquid hydrocarbon, solutions.

It is clearly economically advantageous to operate at ambient temperature and in most cases, if not all, the product will function effectively at this temperature.

- 5 It will also remove metals at higher temperatures if the feedstock is supplied at elevated temperatures.

It is believed that the substrate removes the metals by ion exchange.

- 10 When the substrate loses its activity for removing metals it may either be disposed of without removing the metals or the metals may be removed by means known to those skilled in the art. One such method for removing the metal from the substrate is to contact the metal-loaded substrate with an aqueous solution of an organic  
15 or inorganic acid followed by separation of the aqueous solution containing the metal from the substrate. The acid should be chosen so that the resulting metal salt is soluble in the treating solution.

- Following regeneration in this manner, the substrate  
20 will be obtained in the acid form, i.e., in which M is a hydrogen ion. If the metallic variant is desired it will be necessary to treat the acid form with a solution of the required metallic salt.

- The solution containing metals may be contacted with  
25 the substrate batchwise, or, preferably, continuously by passing the solution over a bed of the substrate mounted in a suitable reactor.

The invention is illustrated by the following Examples:

- A. Preparation of Silica Functionalised with Sodium  
30 Sulphonate Groups

3-Chloropropyltrimethoxysilane (40 ml) was added, at room temperature, to a stirred suspension of 30 - 44 mesh Davison Grade 57 silica (80 g) in toluene (200 ml).

- The reaction mixture was then heated to reflux temperature  
35 for 4 hours under a nitrogen atmosphere. After cooling,

5.

the silica product was isolated, Soxhlet extracted with methanol for 17 hours and then dried in vacuo. To this chloro-silica was added a saturated, aqueous solution of sodium sulphite (300 ml) and the mixture stirred at reflux temperature for 16 hours under a nitrogen atmosphere. After cooling, the silica was isolated by filtration and washed free from residual sodium sulphite with water and finally dried in vacuo. On analysis the sulphur content of this silica was found to be 1.6% wt.

10 B. Preparation of Silica Functionalised with Sulphonic Acid Groups

Sodium sulphonate-silica (prepared as described in A above) was acidified with 0.5 M nitric acid, washed free from residual nitric acid with water and finally dried in vacuo.

On analysis the sulphur content of this silica was found to be 1.8% wt.

Example 1

20 Jet A-1 aviation turbine kerosine containing 235 - 475 parts per billion of soluble copper was pumped, at room temperature and a liquid hourly space velocity of 10, through a 20 ml fixed bed of the sodium sulphonate-silica (prepared as described in (A) above). Samples of the product leaving the reactor were periodically taken and analysed for their copper content. The sample times and the copper content of these samples are given in Table 1.

30

35

5.

Table 1

	Time After Which Sample Was Taken (Hours)	ppb Copper in Sample
5	18	< 10
	66	< 10
	402	< 10
	810	< 10
	978	< 10
10	1142	< 10

Example 2

Jet A-1 aviation turbine kerosine containing 215 - 325 parts per billion of soluble copper was pumped, at room temperature and at a liquid hourly space velocity of 10, through a 20 ml fixed bed of the sulphonic acid-silica (prepared as in B above). Samples of the liquid product leaving the reactor were periodically taken and analysed for their copper content. The sample times and the copper content of these samples are given in Table 2.

Table 2

	Time After Which Sample Was Taken (Hours)	ppb Copper in Sample
25	21	< 10
	45	< 10
30	117	150

C. Preparation of Silica Functionalised with Sodium Sulphonate Groups

A further batch was prepared as described in Example

A. On analysis the sulphur content was found to be 1.77% wt.

Example 3

100 ml of an aqueous solution containing 0.48 g of silver nitrate was shaken with 1.0 g of sodium sulphonate-silica (prepared as described in (C) above) for 18 hours. The silica was then isolated by filtration, washed free from residual silver nitrate with water and finally dried in vacuo. On analysis the silver content of this product was found to be 5.2% wt.

Example 4

100 ml of an aqueous solution containing 0.32 g of rhodium trichloride was shaken with 1.03 g of sodium sulphonate-silica (prepared as described in (C) above) for 18 hours. The silica was then isolated by filtration, washed free from residual rhodium trichloride with water and finally dried in vacuo. On analysis the rhodium content of this product was found to be 1.35% wt.

Example 5

100 ml of an aqueous solution containing 0.47 g of lead nitrate was shaken with 1.04 g of sodium sulphonate-silica (prepared as described in (C) above) for 18 hours. The silica was then isolated by filtration, washed free from residual lead nitrate with water and finally dried in vacuo. On analysis the lead content of this product was found to be 5.6% wt.

Example 6

100 ml of an aqueous solution containing 0.41 g uranyl sulphate was shaken with 1.04 g sodium sulphonate-silica (prepared as described in (C) above) for 18 hours. The silica was then isolated by filtration, washed free from residual uranyl sulphate with water and finally dried in vacuo. On analysis the uranium content of this product was found to be 6.0% wt.



Example 7

100 ml of an aqueous solution containing 0.2 g palladium nitrate was shaken with 1.04 g sodium sulphonate-silica (prepared as described in (C) above) for 18 hours. The silica was then isolated by filtration, washed free from residual palladium nitrate with water and finally dried in vacuo. On analysis the palladium content of this product was found to be 0.13% wt.

Example 8

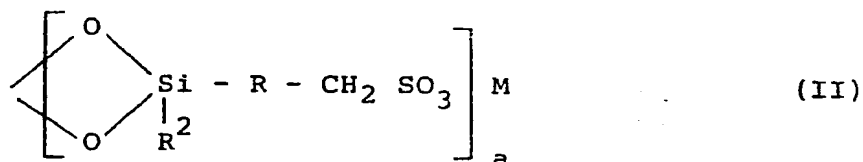
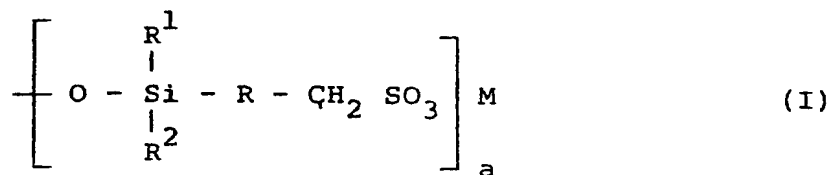
100 ml of a solution of Jet A-1 aviation turbine kerosine containing 1200 parts per million of soluble cobalt was shaken with 1.06 g of sodium sulphonate-silica (prepared as described in (C) above) for 18 hours. The silica was isolated by filtration, washed free from residual cobalt with a series of solvents, i.e., Jet A-1 aviation turbine kerosine, toluene and then methanol, and finally dried in vacuo. On analysis the cobalt content of this product was found to be 0.91% wt.

Example 9

100 ml of an aqueous solution containing 0.6 g mercuric chloride was shaken with 0.93 g of sulphonic acid-silica (prepared as described in (B) above and shown to contain 0.6% wt sulphur) for 18 hours. The silica was isolated by filtration, washed free from residual mercuric chloride with water and finally dried in vacuo. On analysis the mercury content of this product was found to be 0.2% wt.

## Claims:

1. A process for the removal of metals from solution which process comprises contacting the solution with a product, derived from an inorganic oxide containing surface hydroxyl groups, containing groups of general formulae (I) and/or (II):



wherein R is a divalent radical containing up to 20 carbon atoms,  $\text{R}^1$  and  $\text{R}^2$  are halogen atoms, organic radicals containing up to 20 carbon atoms, or hydrolysis products thereof, M is a metallic or hydrogen ion and (a) is an integer corresponding to the valency of M.

2. A process according to claim 1 wherein  $\text{R}^1$  and/or  $\text{R}^2$  are alkoxy groups containing 1 to 3 carbon atoms, R is a di- or tri-methylene group, and M is an alkali metal or hydrogen ion.
3. A process according to either of the preceding claims wherein the inorganic solid containing surface hydroxyl groups is silica, alumina, titania, zirconia, glass,

sepiolite or a zeolitic molecular sieve.

4. A process according to any of the preceding claims wherein the process is operated at ambient temperature.
5. A process according to claim 1 as hereinbefore described with reference to the Examples.
6. Products whenever treated by a process according to any of the preceding claims.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0011484  
Application number  
EP 79 30 2585

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	GB - A - 1 530 039 (BRITISH PETROLEUM CO.)		C 22 B 3/00 B 01 J 20/32 C 07 F 7/08
A	DE - A - 2 522 812 (BRITISH PETROLEUM CO.)		
A	FR - A - 2 383 690 (MERCK PATENT GmbH)		
A	FR - A - 2 275 252 (I. SEBESTIAN)		
A	FR - A - 2 230 405 (I. HALASZ)		
A	US - A - 3 664 967 (R.H. STEHL)		
-----			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 22 B 3/00 B 01 J 20/32 27/02 31/12 C 07 F 7/08
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			& member of the same patent family, corresponding document:
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
The Hague	29-01-1980	JACOBS	

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER: \_\_\_\_\_**

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**